RESEARCH IN THE SYNTHESIS OF RARE EARTH COMPOUNDS AND A STUDY OF THEIR MAGNETIC OPTICAL AND SEMICONDUCTING PROPERTIES

Semiannual Technical Report
30 June 1970 to 31 December 1970

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F. Holtzberg, T. R. McGuire, T. Penney,
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ABSTRACT

During this period we have emphasized the development of an under-standing of the chemical equilbria involved in the synthesis and crystal growth of pure and doped europium chalcogenides. We have also further explored the relationship of defect structures and dopant concentration to the magnetic, optical and transport properties of these materials.

Since nonstoichiometry is a significant factor determining the physical properties of the chalcogenides, vapor-solid equilibrium in EuSe was investigated. Knudsen effusion and mass spectrometric analyses show that EuSe dissociates to yield equal pressures of Eu and Se in the vapor phase. In contrast EuO has been shown to be in equilibrium with only Eu vapor. These thermodynamic data will be very useful in extablishing the conditions for crystal growth.

A study of the reaction between H_2S and Eu_2O_3 was carried out to determine the amount of residual oxygen in EuS as a function of reaction temperature. Samples produced at 1200°C in flowing H_2S were found to contain less than 100 ppm oxygen. Gd doped EuS samples produced under the same conditions are not conducting until treated under a Eu pressure.

Magnetic measurements for the system $Eu_{1-x}Gd_xS$ over the range $x = .03$ to .36 show ferromagnetic properties with an increase in Curie temperature by a factor of three times over that of insulating EuS. The low temperature saturation moment, however, decreases with Gd concentration. This decrease in moment may arise from the development of a canted magnetic structure.

Transport properties in both metallic and semiconducting europium chalcogenides are under investigation. In the former the effort is directed towards understanding the exchange interactions between conduction electrons and the localized spin of the rare earths. In the latter, the purpose is to distinguish between two basic transport processes, hopping and band conductivity. One technique which has been particularly successful is photoconductivity. The results of static and transient photoconductivity measurements in EuSe show that there is thermally activated conduction in the paramagnetic region which increases with increasing magnetic field. The thermally activated conduction may be due to either hopping or quasi-thermal activation to the conduction band.

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INTRODUCTION

The magnetic optical and electrical properties of the semiconducting ferromagnetic europium monochalcogenides have been shown to be critically dependent on electron concentration. The stoichiometric compounds are insulators with resistivities of the order of 10^8 to 10^{10} Ω cm. The electron concentration can be varied by doping with trivalent rare earths, halide ions or by developing vacancies on the anion or cation sites. At concentrations of about 1%, or 10^{19} carriers per cc, the chalcogenides are essentially metallic if compensation does not occur. Since single crystals of the monochalcogenide compounds are grown at very high temperatures (2000-2500°C) in sealed tungsten crucibles, the stoichiometry of the compound will be strongly dependent on the partial pressures and the composition of the vapor species, on the thermal history of the crystal as the temperature is reduced to ambient, and on the inclusion of impurities not segragated during the crystallization process. The concentration of impurities and dopants can be chemically measured to a level of several atomic parts per million using electron probe and mass spectrometric techniques. What cannot be measured readily is the degree of compensation or the vacancy concentration on either lattice site. This study depends critically therefore on the correlation of the conditions used for the growth of single crystals with physical measurements, which can give insight into the nature of the defect structures.

CHEMISTRY

The europium monochalcogenides all exist over a range of stoichiometries. Unlike the oxide which has only been made n-type, the sulfide, selenide and telluride can all be obtained with both n- and p-type conductivity. Estimates of the width of solid solubility in these systems are of the order of 1-4 mole %.[1-4] As a result, single crystals of the undoped compounds can have resistivities varying from 10^{10} - 10^{-3} Ω cm., depending on vacancy concentrations. The vapor solid equilibria vary for the different chalcogenides. Haschke and Eick,[5] using a Knudsen effusion cell and mass spectrometric analysis, found that EuO vaporized according to the reaction

$$4EuO(s) \rightarrow Eu_3O_4(s) + Eu(g)$$
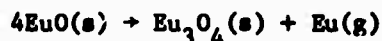
in the temperature range 1334-1758°K.

They also established that Eu_3O_4[6] vaporized according to the equation

$$3Eu_3O_4(s) \rightarrow 4Eu_2O_3(s) + Eu(g)$$

It is clear in the case of the oxide that the composition of the solid solution is dependent only on the partial pressure of the single constituent Eu(g) in the vicinity of the stoichiometric compound. M. Frisch of this laboratory has studied the vaporization of EuSe and finds that within the limits of mass spectrometric measurement the compound is congruently vaporizing, that is, equal pressures of Eu(g) and Se(g) are observed in the vapor phase. In continuation of this work we are presently studying the vaporization of EuS.

The introduction of a trivalent impurity increases the partial pressure of Eu significantly and if equilibrium pressures are not established during crystal growth the resulting doped material can be completely compensated by loss of Eu with resulting Eu lattice vacancies.[4] We hope to obtain the requisite equilibrium data on such systems using Knudsen effusion and mass spectrometric analyses for crystal growth parameters.

In the region of low dopant or vacancy concentration (< 1%) the control of stoichiometry is most crucial since we are dealing here with semiconducting properties, and the physical measurements will reflect the possible existance of magnetic cluster formation or chemical inhomogeneities. In either case the ferromagnetic phase transitions show tailing phenomena which can either be interpreted as short range order within clusters or a spread of Curie temperatures resulting from chemical gradients. In this concentration range the ferromagnetic Curie temperature, T_c and the para-magnetic Curie Weiss Θ can differ by as much as 10°K.

At higher dopant concentrations, where the samples are metallic, T_c and Θ are essentially the same as can be seen for the samples listed in Table II. The conditions for solid solution formation are less critical in this concentration range.

The preparation of chalcogenides by the vapor reaction of the elements has an inherent limitation in that the "high" purity Eu metal always has oxygen contamination of the order of 500-1000 ppm. A study of the reaction of Eu_2O_3 with H_2S[7] was carried out in some detail in order to determine the residual oxygen content as a function of reaction temperature.

At temperatures below 1200°C high purity H_2S gas (total impurity content < 60 ppm. of which oxygen was < 10 ppm) was passed over four nines

Eu_2O_3 contained ٭ a sulfide saturated platinum boat. In the high temperature reactions, the Eu_2O_3 was contained in ٠ vitreous carbon boat which was placed inside a carbon susceptor. This arrangement allowed us to reach temperatures in excess of 2000°C in an H_2S atmosphere. When carbon was used as the container the sulfide samples, which were taken for analysis, were separated from the crucible by a 1/8" thick layer of powdered EuS to avoid sample reaction with the carbon.

The results, in terms of the phases formed and the oxygen content of the products, are summarized in Figure 1 for the low temperature reactions. The phases were identified by x-ray diffraction with a detection sensitivity of only about 5%. The phase relations are described in Figure 1 in terms of the ternary system Eu_2O_3 - EuS and the hypothetical compound Eu_2S_3. The compositions are shown by the larger closed circle in the various isothermal sactions. It can be seen that the initial phase to form is the trivalent oxysulfide Eu_2O_2S, and between 550 and 600°C it and Eu_3S_4 are in equilibrium. It should be pointed out that at 700°, even though Eu_3S_4 and EuS are the phases in equilibrium, there is still a considerable amount of oxygen in the lattice i.e. the composition is off the join between Eu_2S_3 and EuS. Above 900° only EuS can be identified. Its oxygen content, obtained by neutron acitivation analyses, shown in the lower curve in Figure 1, is roughly 100-200 ppm but it drops off to less than 100 at higher temperatures. This represents the total oxygen found in powdered samples and most certainly represants an upper limit in the lattice since no precautions were taken to prevent the adsorption of oxygen from the atmosphere. The analyses results have not as yet been obtained for the samples prepared above 1200°C but microstructural analysis showed single phase, high density EuS.
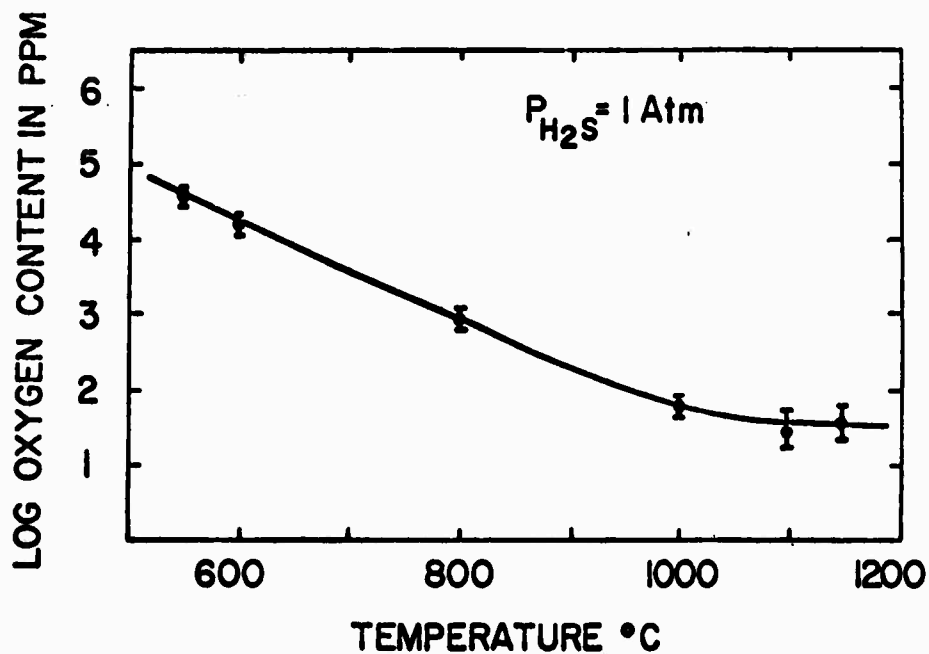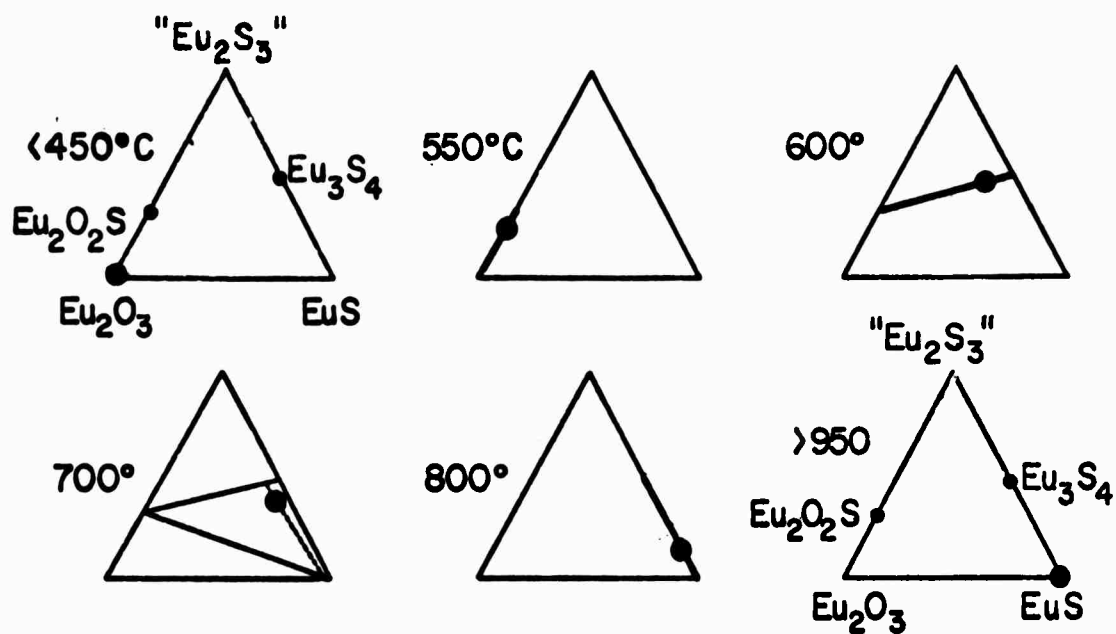
Figure 1: Top: Phase relations in Eu_2O_3-"Eu_2S_3"-EuS systems
Bottom: Oxygen content of EuS after H_2S treatment

TABLE I. DETERMINATION OF THE PHASES IN $Eu_{1-x}Gd_xS$
AS A FUNCTION OF "Eu PRESSURE"

Gd Conc. x in EuS*	"Eu Pressure"** (atm)	ρ_{RT} (Ω cm)	Remarks
0	0	2.0×10^6	single phase
0.02	0	5.5×10^5	single phase
0.05	0	5	single phase
0	0.25 – 0.5	3.8×10^5	single phase
0.0025	0.25 – 0.5	1.6×10^6	single phase
0.02	0.25 – 0.5	1.0×10^6	single phase
0.05	0.25 – 0.5		1% 2nd phase in grain boundries
0	0.5 – 1.0	4.8×10^5	single phase
0.0025	0.5 – 1.0		thin conducting phase in boundries
0.01	0.5 – 1.0		thin conducting phase in boundries
0.02	0.5 – 1.0	1.8×10^{-1}	single phase
0.03	0.5 – 1.0		single phase
0.05	0.5 – 1.0	1.8×10^{-1}	single phase
0.25	0.5 – 1.0		sample melted, 2 phases
0	1 – 2	3.8×10^5	single phase
0.0025	1 – 2		single phase
0.02	1 – 2	2.5×10^5	single phase
0.05	1 – 2		small amount of 2nd phase
0	3 – 5		lost sample
0.0025	3 – 5	1.9×10^5	single phase
0.02	3 – 5	1.1×10^6	single phase
0.07	3 – 5	2.3×10^4	single phase
0.25	3 – 5		∿ 5% 2nd phase in boundries
0	7 – 10	5.2	single phase
0.0025	7 – 10	1.3×10^2	single phase
0.02	7 – 10	highly conducting	single phase
0.05	7 – 10	highly conducting	not homogeneous

*Determined by microprobe analysis
**See text

Another series of experiments was done to obtain a better under-
standing of the relationship between the transport properties and compensation
by adjusting the Eu metal concentration in Gd doped EuS. The experimental
procedure consisted of coprecipitating the hydroxides of Eu and Gd in various
proportions converting to the sesquioxide at 600° in vacuum, then to the
monosulfide in an H_2S atmosphere at 1200°C. These mixed compositions were
than reacted at 1800° in various pressures of Eu vapor. This was done by
sealing in tungsten crucibles which contained various amounts of Eu-metal.
The "europium pressure" was estimated by assuming all the free europium was
in the vapor phase at 1800° - an assumption which may not be correct for the
higher concentrations. Thus, the pressures listed in Table 1 should not be
taken as exact but since only the amount of Eu-metal added was varied, the
relative pressures are significant.

From these results it can be concluded that Gd can be present in
the EuS lattice without contributing any conduction electrons because it is
compensated by an europium vacancy. As the Eu vacancies are filled by the
treatment with Eu vapor, the conductivity is seen to increase and at the
highest Eu-pressure (5-10 atm), conductivity is also seen in the samples free
of Gd. It is assumed that in this region sulfur vacancies are formed. It
appears that a critical Eu-pressure of between 5 and 10 atm is needed to
remove compensation under the conditions of this experiment. Currently, samples
in this range are being analyzed.

Magnetic Moment Studies

Substituting Gd^{+3} for Eu^{++} in the $Eu_{1-x}Gd_xS$ system adds conduction

electrons and metallic conduction is observed for x > .01. The introduction
of conduction electrons gives rise to an indirect exchange[8] where the ferro-
magnetic exchange is enhanced for x < 0.5 and for x > 0.5 antiferromagnetic
characteristics become predominant. This section discusses the ferromagnetic
properties of the system in the composition interval $0.03 \leq x \leq 0.34$.

Both Eu^{2+} and Gd^{3+} have a half filled 4f shell with a spin only
moment of $7\mu_\beta$. Thus as magnetic atoms they are identical but because of the
difference in ion charge the energy levels of the various shells have different
values. The structure of $Eu_{1-x}Gd_xS$ is fcc and the lattice sites of the
magnetic atoms are crystallographically equivalent.

Table II summarizes the magnetic properties we have thus far obtained.
The first two columns are from the magnetic susceptability, χ, in the para-
magnetic region which follows the Curie Wiess law $\chi = \frac{C_M}{T-\theta}$ where C_M is
proportional to the average effective magnetic moment squared and θ, the
paramagnetic Curie temperature, is a measure of the exchange interactions
in the material. The values listed for the Curie temperature T_c and the
saturation moment σ_o are obtained from analysis of measurements in the
magnetically ordered region where a spontaneous moment exists.

Inspection of the table shows: 1) the value of C_M is close to
theoretical ($C_M = 7.87$ for an atomic moment of 7 Bohr magnetons) for all
compositions. It is not clear what the small decrease in C_M is due to in
the higher Gd concentration region. We plan to do a more detailed study of
the functional relationship of C_M with composition. 2) With the addition of
as little as 3% Gd both θ and T_c increase almost a factor of three which we
attribute to indirect exchange, either 4f-5d of 4f-6s or both if the

TABLE II. MAGNETIC DATA FOR $Eu_{1-x}Gd_xS$ IN THE
CONCENTRATION RANGE $0.03 \leq x \leq 0.34$

Material	C_M	Θ (°K)	T_c (°K)	σ_o (emu/gm)
EuS	7.85	19	16.5	212
$Eu_{.97}Gd_{.03}S$	7.63	52	49.5	206
$Eu_{.915}Gd_{.085}S$	7.59	52	45.0	188
$Eu_{.80}Gd_{.20}S$	7.55	45	44.5	168
$Eu_{.66}Gd_{.34}S$	7.55	30	35.0	135

d-s bands overlap. 3) The values of Θ and T_c are in substantial agreement indicating well behaved ferromagnetic properties. Earlier measurements[9] indicated substantial differences where $T_c << \Theta$, but this was probably due to sample inhomogeneities. 4) The saturation magnetic moment values (σ_o) decrease almost linearly with composition (x). This means that a complex magnetic structure exists in these materials. As pointed out above Gd^{3+} and Eu^{2+} are magnetically identical and have the expected effective moment in the paramagnetic state. Consequently the ferromagnetic moment σ_o would be expected to remain constant over some range of compositions. Since this is not so we suggest two models to explain the data. The first model involves an inhomogeneous magnetic structure where Eu^{2+} ions are spin parallel and are the only contributors to the measured moment. The Gd^{3+} ion moments are antiparallel and form antiferromagnetic clusters. The second model is simply a canted arrangement of atomic moments where two equivalent sublattices form at an angle to each other giving a reduced moment which is the vector sum. We favor the canted model at the present time based on preliminary analysis of high field moment measurements.

Our current program is to extend our detailed knowledge of this system over a greater range of compositions and to other systems. We show in Figure 2 a new EuS composition containing La^{3+} instead of Gd^{3+} ($Eu_{.99} La_{.01} S$). The La^{3+} serves the same function as Gd^{3+} in contributing conduction electrons but it has zero magnetic moment and therefore simplifies the interpretation of the data because there are less exchange interactions to consider. We see in Figure 2 that the Curie Weiss law holds between 60 and 300°K with a Θ intercept of 42°K. From the low temperature data we obtain $T_c \sim 39°K$, but it will be noted that there is a tail-like shape to the magnetization curves. This tail-like
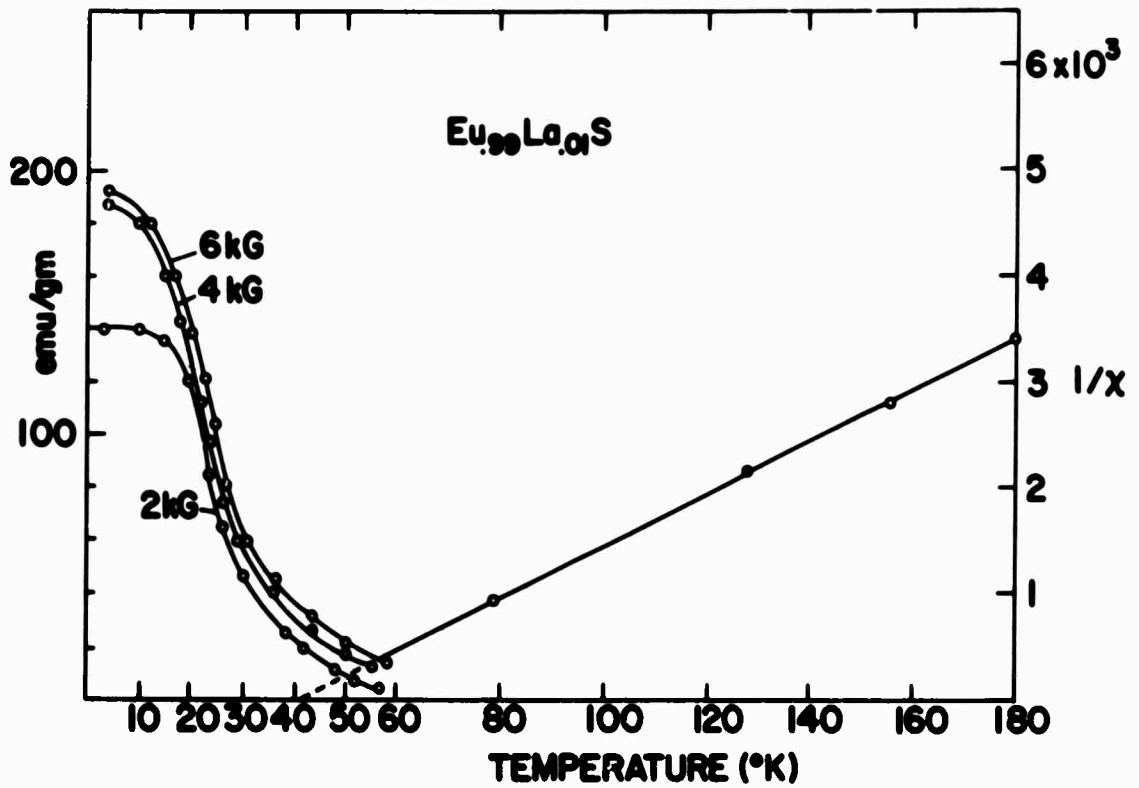
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Figure 2: Magnetization per gram, σ, vs field at 4.2°K and reciprocal
susceptibility, 1/χ, vs temperature

characteristic seems to occur in low doping compositions $x \leq .01$ and its study represents an important part of our future work.

Transport Properties of Europium Chalcogenide

It has been found convenient to seperate the europium chalcogenides into two major categories, depending on dopant concentration. For $Eu_{1-x}D_x$ Ch where Ch is the chalcogenide and D is the dopant, if $x \lesssim 0.01$ the material in general has semiconducting properties, whereas if $x \gtrsim 0.01$ metallic behavior is observed. We are presently carrying out experiments in both regions.

In the metallic region, our purpose is to try to understand and measure the exchange interaction between free electrons and the localized spin of the rare earth ion. The experiment consists of measuring the resistivity, Hall effect, and thermoelectric power of EuS:Gd, GdS and LaS single crystals as a function of temperature. The Hall effect and thermoelectric power yield, on the assumption that a simple parabolic band description is valid, the free carrier number and a rough measure of the Fermi energy E_F. An estimate of the effective mass can then be made. The temperature dependence of the resistivity can be analyzed to obtain a value for the exchange interaction I_{c-f} between the conduction electrons and the localized ionic spin.[10] This is accomplished with the use of the relation[11]

$$\rho_\infty = 4.3 \times 10^{-4} \left(\frac{10^{23}}{N}\right) S \ (S+1) \ \frac{I_{c-s}}{E_F}$$

where ρ_∞ is the magnetic contribution at high temperatures, N is the number of magnetic ions/cc and S the spin of the magnetic ion. We expect to obtain

large differences between I_{c-f} in EuS:Gd and GdS and no magnetic effect in
LaS, since the latter contains no localized spins other than accidental
impurities. The former two materials differ in that present evidence indicates
that the free carriers are s-like in doped EuS and d-like in GdS. The
temperature dependence of the resistivity and the Hall effect has been measured
in both EuS:Gd and GdS, although the Hall signals in GdS are $\lesssim 10^{-8}$ volts,
and thus will require further study. We have recently completed a rather
tedious and lengthy calibration of thermoelectric power apparatus and these
measurements are now in progress.

In the semiconducting region, the problems associated with measuring
and interpreting transport properties are more severe, first because either
chalcogen or rare earth defects, or both contribute to conduction as well as
trivalent rare earth dopants, and because in many cases only the resistivity
is measurable.

Since a knowledge of the specific composition is necessary to relate
carrier number to transport and magnetic properties, a series of homogeneous
samples $Eu_{1-x}Gd_x S$ containing accurately known amounts of trivalent rare earths
were prepared under varying Eu pressures. Thermoelectric power and resistivity
were studied near and above room temperature. It was concluded that the
samples measured fell into two general classes. The majority were p-type with
activation energies varying from 0.26 to 0.49 ev and resistivities greater
than 10^5 Ω cm. The remaining samples were highly conducting and n-type,
representing materials with large Gd concentrations and/or anneals under high
Eu pressure. Although no specific relationship between transport and method
of preparation has evolved, the results suggest conditions for the observation
of n-type conductivity in EuS.

The resistivity of the semiconducting europium chalcogenide is characterized by an anomolous magnetic field dependent maximum near the ferromagnetic transition temperature. In EuS and EuSe this effect has been explained in terms of electron hopping between "magnetic impurity states"[12] whereas the metal insulator transition observed in $EuO:Eu$[13] below the Curie temperature is believed to be due to a carrier concentration change associated with the autoionization of the He-like oxygen vacancies.[14] In order to test the hopping descriptions of transport, a study of the frequency dependence of the conductivity, $\sigma(\omega)$, was undertaken in EuS:La. Whereas, $\sigma(\omega) \propto \dfrac{1}{1+\omega^2\tau^2}$ for metallic conduction, i.e. $\sigma(\omega)$ starts with its d.c. value at low ω and decreases with increasing ω, accepted theories of hopping conductivity predict that σ increases with ω, i.e., $\sigma(\omega) \propto \omega^n$ [15] where n is in despute. Very careful a.c. experiments performed on EuS:La, whose d.c. resistivity changes by $\sim 10^8$ near the Curie temperature, indicated no frequency dependence up to 10^6 hertz. This would seem to support free electron-like conduction, but preliminary infra-red absorption (which measures $\sigma(\omega)$) demonstrates that a frequency dependence does exist in these materials, albeit very complicated and not as yet understood. Further I-R investigations are in progress (supported by ONR contract N00014-70-C-0272).

Another part of our effort has been to study the effects of changes in carrier concentration on the Mössbauer spectrum in EuO:Eu. It is expected that if the metal-insulator transition reflects a change in carrier number, the isomer shift (which measures the s-electron charge density at the nucleus) should change. This effect has been observed[16] and is consistent with our recent measurements of the high and low temperature Hall effect in this material.

Photoconductivity Mechanisms in the Magnetic Semiconductor EuSe

Thermally activated photoconduction has been observed in the paramagnetic phase of EuSe (T_N = 4.6°K) by both steady state and transient measurements. The transient measurements show that it is the photomobility and not the relaxation which is activated. The photoconductive decay tends to be long, nonexponential, sample dependent and independent of temperature and magnetic field, below 100°K. The activation energy (several hundredths of an eV) is at least partially magnetic in origin, for it can be decreased significantly by a magnetic field. Of particular interest is the similarity of the results to the dark conductivity of 1% Gd doped EuSe in the paramagnetic phase.[17] This connection has been previously noted with respect to the steady state photoconduction.[18]

It appears that photoelectrons in undoped EuSe conduct in much the same manner as do impurity electrons in doped EuSe. In doped material, activated conduction in the paramagnetic region has been explained in terms of hopping between impurity sites.[12,19] An electron, bound near an impurity, causes nearest and next nearest neighbor Eu spins to be partially aligned due to the strong s-f exchange interaction, lowering the electron exchange energy. An electron, bound to an impurity by the coulomb interaction, thus has an additional binding energy, magnetic in origin. The result is a magnetic impurity state (MIS). In the model, it is the magnetic binding energy which must be overcome in hopping, but it is the Coulomb energy which causes the localization to begin with.

Since our undoped material has impurities in concentration 10^{-3} - 10^{-4}, it is natural to construct a similar defect model for photoconductivity.

In this model, electrons are excited from localized f levels in the band gap to f-hole d-electron exciton states degenerate with the s-band.[12,20] The exciton breaks up and the electron rapidly relaxes to the bottom of the conduction band and then to an excited state of a deep defect or to a shallow defect.

Activated conduction then occurs by hopping in the shallow states or by thermal excitation to the band. Conduction ends when the electron relaxes to a deep defect state which acts as a recombination center. Spin clusters form around the occupied defect states, that is they are MIS states similar to those proposed for doped material. The activated conduction will be magnetically sensitive just as in the case with doped material.

In this model the long, temperature and magnetic field independent, photodecay results from the decay of an electron in a shallow level associated with one defect to a deep level associated with another defect. Since there will be a distribution in space between defects there will be a distribution in decay times. Since the relaxation is between defects, it will be slow.

For steady state photoconductivity we may write,

$$(I_{dc}/V) \ (\ell/\omega) \ (E/P) = \Sigma_i \ \beta_i \ \mu_i \ \tau_i,$$

where I_{dc} and V are the steady state current and voltage. ℓ and ω are the sample length and width. E is the photon energy and P the power per unit area of radiation at the sample. β_i, μ_i and τ_i are the quantum efficiency, mobility and lifetime for a component, i, of the photo current. A similar expression,

$$(I_T/V) \ (\ell/\omega) \ (E/W) = \Sigma_i \ \beta_i \ \mu_i,$$

may be written for the transient case, where a pulse of light short with respect to the lifetime τ_1 is used. I_T is the current immediately following the pulse and W is the energy per unit area at the sample.

Transient photoconductivity measurements have been made using a xenon flash which has 0.8 of its energy in 10^{-5} sec. or a dye laser with a 2×10^{-6} sec. pulse.

The current amplitude at 10^{-5} sec. is taken as a measure of $\beta\mu$, and the time, τ', to fall to 1/e of that value is its initial decay after the pulse. The results are shown in Figure 3 for both white flash and dye laser excitation.

The data of Figure 3 shows a number of interesting results. The $\beta\mu$ product is thermally activated, while the response time, τ' is constant below 80°K. The activation energy is similar to that of the d.c. photocurrent measurements and the dark conductivity of Gd doped EuSe in the same temperature range.[17,18] Also, the $\beta\mu$ product increases with an external magnetic field, H, while τ' does not. The model described earlier is in agreement with these results since it predicts a thermally activated mobility and temperature independent response time, τ', equal to the lifetime, τ.

From these results and others presented in reference 20 we conclude that the final state of the optical absorption (f-d exciton) lies degenerate with, or above, the shallow defect states responsible for photoconduction. A shallow defect state will trap an electron which then causes a spin cluster to form around it. The result is an additional magnetic binding energy exactly like that proposed for Gd doped EuSe. Conduction then occurs either by hopping within the shallow defect states or by thermal excitation to the band. Conduction ends when the electron relaxes to a deep defect state.
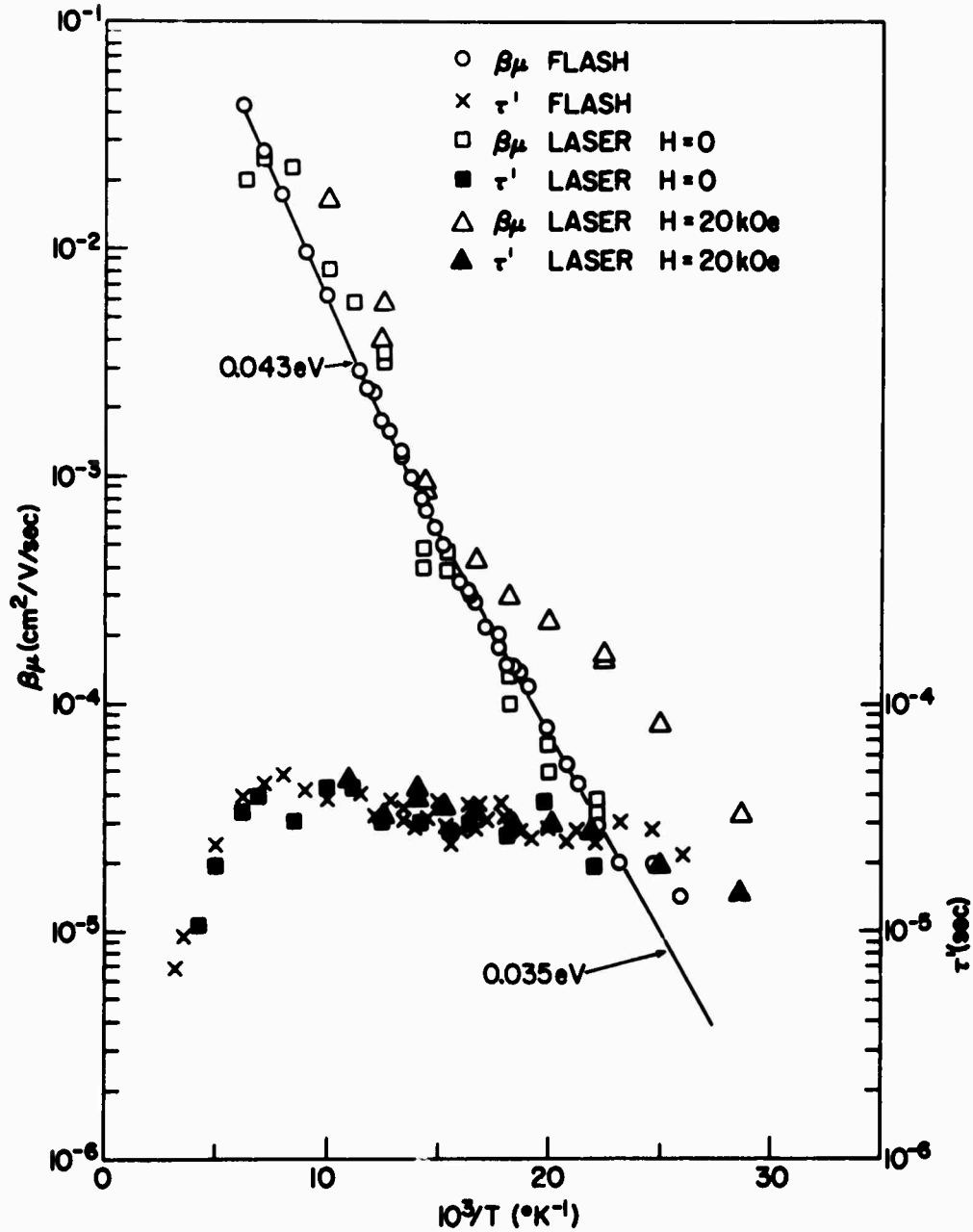
Figure 3: $\beta\mu$ and τ' vs inverse temperature for EuSe. White light source is a Xenon flash at 10^{-4} J/cm^2. Dye laser source is 2.12 eV at 3×10^{-5} J/cm^2. Bias is 100V. $\beta\mu = 0.1$ corresponds to 10^{-3} amp for the laser with 100V bias. Current and decay are measured at 10^{-5} sec. The slopes are indicated in eV.

the conditions for the above model are as follows. In Gd doped EuSe, the deep defects (Gd) must be sufficiently numerous ($\sim 10^{-2}$) so that their wave functions overlap enough for hopping but not so much that impurity banding takes place. There must be some compensation so that there are empty sites to hop to. In undoped EuSe, the deep defects must be sufficiently scarce ($10^{-3} - 10^{-4}$) so that hopping is unimportant. However, shallow defects with larger wave functions should be present in an amount ($10^{-3} - 10^{-4}$) so that impurity banding is not possible and hopping may or may not be possible. In the latter case, the electrons conduct by excitation to the band. Some compensation is required so that holes in deep states will be available for recombination and their number will be independent of the light intensity.

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(abstract continued)

Transport properties in both metallic and semiconducting europium chalcogenides are under investigation. In the former the effort is directed towards understanding the exchange interactions between conduction electrons and the localized spin of the rare earths. In the latter, the purpose is to distinguish between two basic transport processes, hopping and band conductivity. ( ) One technique which has been particularly successful is photoconductivity. The results of static and transient photoconductivity measurements in EuSe show that there is thermally activated conduction in the paramagnetic region which increases with increasing magnetic field. The thermally activated conduction may be due to either hopping or quasi-thermal activation to the conduction band.

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13. ABSTRACT

During this period we have emphasized the development of an understanding of the chemical equilbria involved in the synthesis and crystal growth of pure and doped europium chalcogenides. We have also further explored the relationship of defect structures and dopant concentration to the magnetic, optical and transport properties of these materials.

Since nonstoichiometry is a significant factor determining the physical properties of the chalcogenides, vapor-solid equilibrium in EuSe was investigated. Knudsen effusion and mass spectrometric analyses show that EuSe dissociates to yield equal pressures of Eu and Se in the vapor phase. In contrast EuO has been shown to be in equilibrium with only Eu vapor. These thermodynamic data will be very useful in extablishing the conditions for crystal growth.

A study of the reaction between H_2S and Eu_2O_3 was carried out to determine the amount of residual oxygen in EuS as a function of reaction temperature. Samples produced at 1200°C in flowing H_2S were found to contain less than 100 ppm oxygen. Gd doped EuS samples produced under the same conditions are not conducting until treated under a Eu pressure.

Magnetic measurements for the system $Eu_{(1-x)}Gd_xS$ over the range x = .03 to .36 show ferromagnetic properties with an increase in Curie temperature by a factor of three times over that of insulating EuS. The low temperature saturation moment, however, decreases with Gd concentration. This decrease in moment may arise from the development of a canted magnetic structure.

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